

PATENT SPECIFICATION

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(54) METHOD FOR ADJUSTING THE COAGULATION POINT OF CARBOXYLATED LATTICES



(19)

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of the Federal Republic of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

(72) The "heat coagulant"-process is based on adjusting the thermosensitivity of natural rubber latex, synthetic rubber latex or polyacrylate dispersions by the addition of heat sensitizing agents such as polyvinylmethyl ethers, polyether thioethers or organopolysiloxanes so that the latex mixture coagulates suddenly when heated to a certain temperature known as its coagulation point but remains stable over a prolonged period at room temperature without undergoing any change in its viscosity. This method is very suitable for the production of foamed rubber and dip moulded articles as well as for achieving a uniform bonding of fibre fleeces.

(73) Upon impregnating fibre fleeces the binder normally migrates when the fleece is dried if the surfaces of the impregnated fleece are heated alternately or simultaneously. Migration results in severe loss of binder from the centre of the fleece so that the binding between the fibres at the centre is weakened and, at the same time, the accumulation of binder in the outer zones results in a product with a very stiff hand.

(74) This is particularly undesirable in highly compacted non-woven textiles which are split after drying and used as a base material for the production of synthetic leather, because the split pieces then differ from each other in their technological properties. These disadvantages are substantially obviated by using thermosensitive binders.

A pronounced textile hand of the kind which is desired, e.g. for non-woven textiles

used as interlinings, also can only be achieved with the aid of a thermosensitive dispersion.

Another advantage lies in the fact that the bonded fleece produced in this way can be passed over squeezing rollers after coagulation of the binder and thereby freed from most of the serum, with the result that the drying capacity of the plant is correspondingly increased and saving in energy costs is achieved. Furthermore, in the case of needle felt floor coverings made of undyed fibres, it is possible to apply a dye liquor after coagulation without the binder being thereby washed out, and the felt can then be steamed without first being dried (continuous process). Exceptionally brilliant colours can be obtained in this way.

The usefulness of a synthetic resin dispersion for the "coagulant" process depends, however, on the coagulation point of the thermosensitive mixture and the degree to which it remains constant over several days. In addition, the properties of the wet gel and dry gel must conform exactly to the requirements of the processing technique employed.

The desired coagulation point, in particular, varies for different fields of application. For highly compacted non-woven textiles which are split after application of the thermosensitive binder, the coagulation point should be low in order to avoid as far as possible any migration during heating up to the coagulation temperature. On the other hand, a slightly higher coagulation point is often desired in order to achieve a certain controlled migration during the heating up period and thereby reduce the quantity of binder required.

It is known that the coagulation point of synthetic rubber latices can be adjusted as desired within a wide temperature range after thermosensibilisation. According to German Auslegeschrift No. 1,243,394, the coagulation point can be predetermined if the latex is prepared by polymerisation of the monomers in the presence of an emulsifier combination of

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2 to 8% by weight (based on the monomers) of a water-soluble alkali metal sulphonate or sulphate containing 12 to 18 carbon atoms and at least 0.5% by weight (based on the monomers) of a non-ionogenic emulsifier which has a cloud point above 75°C and/or a non-ionogenic emulsifier having a cloud point below 75°C. The non-ionogenic emulsifier with the high cloud point lowers the coagulation point whereas the non-ionogenic emulsifier with low cloud point raises the coagulation point. Furthermore, it has been disclosed in German Auslegeschrift No. 1,243,394 that the coagulation point of heat sensitizable synthetic rubber latices of butadiene, styrene, acrylonitrile and methacrylic acid falls with increasing acrylonitrile content.

When bonding non-wovens with heat sensitized synthetic rubber latices, the impregnated textiles are in most cases passed between squeezing rollers and the rubber is coagulated and subsequently washed free from emulsified so that the serum accumulates in the effluent water. It is therefore desirable to use only biologically easily degradable emulsifiers for the production of synthetic rubber latices which can be made thermosensitive and the production of the thermosensitive mixture.

It is an object of this invention to provide a method by which the coagulation point of heat sensitizable rubber latices can be reduced without the aid of emulsifiers which are not biologically degradable and the coagulation point, once adjusted, can be kept constant over a prolonged period.

This invention thus relates to a process for the reduction of the coagulation point of a rubber latex which is free from non-ionogenic emulsifiers and which contains the following copolymerised components:

- 1) 20 to 60 parts by weight of styrene,
- 2) 40 to 80 parts by weight of butadiene,
- 3) 1 to 6 parts by weight of acrylic acid and/or methacrylic acid,
- 4) 0 to 15 parts by weight of acrylonitrile and/or methacrylonitrile,
- 5) 0 to 5 parts by weight of acrylamide and/or methacrylamide and
- 6) 0 to 5 parts by weight of N-hydroxymethyl- and/or N-alkoxymethyl-acrylamide and/or -methacrylamide,

in which composition the sum of components 5 and 6 must be at least 1 part by weight, in which only ionogenic emulsifiers which readily undergo biological degradation are used for the preparation of the latex, in which a heat-sensitizing agent is added to the latex, the quantity of components 4, 5 and 6 being calculated so that, after addition of the heat sensitizing agent, a coagulation point of 35 to 60°C which remains constant over a prolonged period is obtained.

The invention is thus based on the finding that the coagulation point of the latex can be reduced below those of latices of copolymers of butadiene, styrene and (meth)acrylic acid solely by the quantity of the hydrophilic monomers (meth)acrylonitrile, acrylamide or methacrylamide and hydroxy- or alkoxy-methyl(meth)acrylamide copolymerised and that this can be achieved in a specific and reproducible manner. Once adjusted, the coagulation point remains stable over a prolonged period.

The higher the proportion of hydrophilic monomers, the lower is the coagulation point. (Meth)-acrylonitrile has a much weaker action than (meth)-acrylamides or their derivatives mentioned above.

Only anionogenic emulsifiers need then be added for polymerisation, and for reasons of environmental protection the kind which are biologically degradable are used, preferably sulphonates or sulphates.

The addition of copolymerisable amides or their N-substitution products is of major importance for the ability of the synthetic rubber latices to be thermosensitizable, because these comonomers are largely responsible not only for the coagulation point itself but also for its constancy over a prolonged period while copolymerisable nitriles in addition determine the coagulation point itself. Increasing quantities of nitrile and amide or their N-substitution products, shift the coagulation point to lower temperature regions, the nitrile having a weaker effect in this respect than amides and their N-derivatives.

This simple principle of the method of adjustment of the coagulation point is completely independent of the method employed for production of the synthetic rubber latices and affords special advantages, in particular for the production of synthetic rubber latices which undergo self-cross-linking. It was found that copolymerisable N-methylamides either in the free and/or the masked form are very similar in their behaviour to copolymerisable amides in latices which can be heat sensitized.

On the principle outlined above, it is possible to vary the elongation at break of the polymer according to the particular requirements in the field for which it is used by varying the quantity of groups which undergo self-cross-linking (N-methylol- and/or ethenified N-methylol(meth)acrylamides) while the coagulation point can be kept constant or varied as required by suitable choice of the quantity of nitrile groups in the polymer, and the constancy of the coagulation point can be approximately ensured over a prolonged period of time.

The synthetic rubber latices used according to the invention may be prepared by polymerisation of the monomers in aqueous emulsion in the presence of at least one alkali metal and/or ammonium sulphate and/or alkali

metal and/or ammonium sulphonate containing 10 to 18 carbon atoms.

The method according to the invention therefore has the advantage that the coagulation point can easily be adjusted as desired, simply by adjusting the nitrile/amide ratio without altering the polymerisation process or composition of the mixture.

The initiators used are in particular organic peroxy-compounds such as acylhydroperoxides, diacylperoxides, alkylhydroperoxides, arylalkylhydroperoxides, dialkylperoxides, diarylalkylperoxides and esters such as tert-butyl perbenzoate used either alone or in combination with suitable reducing agents. The quantity of initiator used is generally within the limits of 0.01 to 5% by weight, based on the total quantity of monomers. Initiation by means of inorganic peroxy compounds would obviously in general result in poorer coagulation characteristics due to stabilisation of the polymer chain ends by hydrophilic sulphate groups.

It is usually advisable to carry out the polymerisation in the presence of promoters such as, for example, small quantities of inorganic metal salts the cations of which are capable of existing in more than one valency stage, e.g. salts of copper, manganese, iron, cobalt or nickel.

The effects which can be achieved with the aid of promoters can often be substantially enhanced by the addition of complex forming compounds such as cyanides, fluorides, hexametaphosphates, diphosphates and in particular ethylene-diaminotetraacetic acid.

Chain transfer agents such as tetrachloromethane, trichlorobromomethane, tetrachloroethane, methyl chloride, alkyl and cycloalkyl alcohols, alkylmercaptans and diisopropylxanthogenates may also be used.

Preparation of the thermosensitizable synthetic rubber latices is generally carried out by emulsifying the total quantity of monomers in an aqueous emulsifier solution and inducing polymerisation by the addition of an initiator and if indicated a suitable reducing agent. Aqueous emulsifier solution may be added continuously or intermittently during polymerisation. The polymerisation temperature employed is generally 5 to 60°C.

Dispersions with solids contents of from 1 to 70% by weight can be prepared in this way although it is customary to use synthetic rubber dispersions with solids contents of from 30 to 65% by weight.

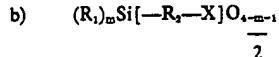
Organopolysiloxanes of the kind described in German Offenlegungsschrift No. 1,494,037 are preferably used for thermosensitisation.

These polysiloxanes consist of two units of the formula



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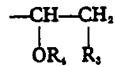
and 1 to 20 units of the formula



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in which

X represents a group of the formula



R₁ represents hydrogen or an alkyl or aryl group,

R₂ represents an alkylene group which may contain oxygen,

R₃ represents a polyether group,

R₄ represents R₁ or an acyl group,

m represents 1 or 2 and

n represents 1, 2 or 3.

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These organopolysiloxanes are generally used in quantities of 0.1 to 10% by weight (based on the solids content).

The synthetic rubber latices used in the examples are prepared as follows:

A solution of 2.0 parts by weight of a sodium sulphonate of a mixture of long chain paraffin hydrocarbons containing 10 to 18 carbon atoms, 0.1 part by weight of tetrasodium diphosphate and 0.05 parts by weight of tetrasodium ethylene diaminotetraacetate (Triton B—Registered Trade Mark) in 120 parts by weight of water is introduced into a 40 l autoclave equipped with crossblade agitator. 0.05 parts of a 10% aqueous solution of iron(II) sulphate heptahydrate are then added and the total quantity of methacrylic acid and of the (meth)acrylamide or its N-hydroxymethyl and/or N-alkoxymethyl derivatives is dissolved in the reaction mixture. The mixture is then adjusted to pH 3.5 with 10% aqueous ammonia solution. Styrene, 0.3 parts by weight of tert-dodecylmercaptan and optionally (meth)acrylonitrile are added. The autoclave contents are evacuated and butadiene is then forced in after the pressure has been equalized with nitrogen. When the stirred emulsion has been heated up to 35°C, polymerisation is started by forcing into the mixture 0.05 parts by weight of tert-butyl hydroperoxide in 1 part by weight of styrene and 0.025 parts by weight of sodium formaldehyde sulphoxylate dihydrate (Rongalit C—Registered Trade Mark) in 5 parts by weight of water. At a solids concentration of 15 g and 30 g, respectively, 1.25 parts by weight (in the case of dispersions which are not self-cross-linking) or 1.5 parts by weight (in the case of self-cross-linking dispersions) of sodium paraffin sulphonate (C₁₀—C₁₂) and 0.0125 parts by weight of Rongalit C in 10 parts by weight of water are added and the

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polymerisation temperature is gradually raised to 50°C. When a final concentration of 41 g has been reached, an emulsion of a phenolic age resister is added and the latex is degassed at 40°C. It is then adjusted to pH 6 to 7 with 10% aqueous ammonia solution.

Latices which are not self-reactive are thermosensitized by the following composition (I):

- 10 100 parts by weight of synthetic rubber dry substance,
- 100 parts by weight of water,
- 10 parts by weight of 20% aqueous solution of sodium paraffin sulphonate ($C_{10}-C_{18}$),
- 10 parts by weight of 15% aqueous solution of 20 times ethoxylated cetyl alcohol,
- 2 parts by weight of organopolysiloxane,
- 40 parts by weight of 10% aqueous ammonium chloride solution and
- 40 parts by weight of vulcanisation paste.

Self-cross-linking synthetic rubber latices are sensitized by the following composition (II):

- 100 parts by weight of synthetic rubber dry substance,
- 50 parts by weight of water,
- 10 parts by weight of 20% aqueous solution of sodium paraffin sulphonate ($C_{10}-C_{18}$) and
- 2 parts by weight of organopolysiloxane.

Example 1

A copolymer of 60 parts by weight of butadiene, 30 parts by weight of styrene, 3 parts by weight of methacrylic acid and 1 part by weight of methacrylamide which has been thermosensitized according to composition I has a coagulation point of 53°C which remains constant for 7 days.

Example 2

A copolymer of 60 parts by weight of butadiene, 28 parts by weight of styrene, 8 parts by weight of acrylonitrile, 3 parts by weight of methacrylic acid and 1 part by weight of methacrylamide thermosensitized according to composition I is found to have a coagulation point of 39°C which remains approximately constant for 7 days.

Example 3

The same as Example 2 except that 1 part by weight of methacrylamide is replaced by the corresponding quantity of butadiene. This copolymer dispersion is found to have a coagulation point of 38°C which rises to 44°C during one week. Binders having a similar composition but not containing carbonamide groups coagulate even while the mixture is being prepared. The coagulation point rises

to over 70°C when the quantity of ammonium chloride is reduced.

Example 3 thus demonstrates the necessity for the presence of amide groups in the polymer for making the dispersions capable of being sensitized and ensuring the constancy of the coagulation point. With the addition of only 1 part by weight of methacrylamide the mixture is already sufficiently sensitive and its coagulation point remains constant for 7 days even without nitrile groups. A comparison of the dispersions mentioned in Examples 1 and 2 illustrates the possibility of shifting the coagulation point by the incorporation of nitrile groups, while still obtaining a thermosensitive mixture and constant coagulation point.

Example 4

A copolymer of 60 parts by weight of butadiene, 26 parts by weight of styrene, 10 parts by weight of acrylonitrile, 3 parts by weight of methacrylic acid and 1 part by weight of N-hydroxymethyl-acrylamide which has been thermosensitized according to composition II can be coagulated at 41°C. This coagulation point also remains approximately constant for 7 days. Elongation at break: 950 to 1050% (DIN 53 455).

Example 5

In the dispersion described in Example 4, 1 part by weight of N-hydroxymethyl-acrylamide is replaced by 1 part by weight of N-methoxymethyl-methacrylamide. In this case again the coagulation point of 43°C remains approximately constant for 7 days. Elongation at break: 800 to 900% (DIN 53 455).

Examples 4 and 5 thus illustrate that applying the principle according to the invention, dispersions with excellent thermosensitivity can also be obtained if the amide groups are hydroxymethylated or alkoxyethylated. (Meth)acrylamides and their N-hydroxymethyl and N-alkoxymethyl derivatives are similar in their behaviour since the coagulation points lie within the same temperature range.

Example 6, finally, demonstrates that the coagulation point can be much more effectively lowered by the N-methoxymethyl-methacrylamide content than by the acrylonitrile content.

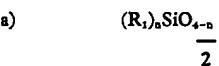
Example 6

A copolymer of 60 parts by weight of butadiene, 31 parts by weight of styrene, 3 parts by weight of acrylonitrile, 3 parts by weight of methacrylic acid and 3 parts by weight of N-methoxymethyl-methacrylamide which has been thermosensitized according to composition II can be coagulated at 46°C. This coagulation point also remains virtually constant for 7 days. Elongation at break: 300 to 400% (DIN 53 455).

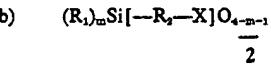
A comparison of Examples 4, 5 and 6 shows how, given approximately the same coagulation point, the elongation at break can be adjusted as desired by the quantity of α,β -monoolefincally unsaturated N-hydroxymethyl carboxylic acid amides or N-alkoxymethyl carboxylic acid amides and the nitrile content.

WHAT WE CLAIM IS:—

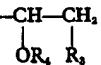
1. A process for reducing the coagulation point of a rubber latex which is free from non-ionogenic emulsifiers and contains the following components in polymerised form:
 - 1) 20 to 60 parts by weight of styrene,
 - 2) 40 to 80 parts by weight of butadiene,
 - 3) 1 to 6 parts by weight of acrylic acid and/or methacrylic acid,
 - 4) 0 to 15 parts by weight of acrylonitrile and/or methacrylonitrile,
 - 5) 0 to 5 parts by weight of acrylamide and/or methacrylamide and
 - 6) 0 to 5 parts by weight of N-hydroxymethyl- and/or N-alkoxymethyl-acrylamide and/or -methacrylamide,
- in which the sum of components 5 and 6 must be at least 1 part by weight, in which only anionogenic emulsifiers of the kind which can easily be biologically degraded are used in the preparation of the latex in which a heat-sensitising agent is added to the latex, the quantity of components 4, 5 and 6 being calculated so that, after the addition of the heat sensitising agent, a coagulation point of 35 to 60°C which remains constant over a prolonged period is obtained.
2. A process as claimed in claim 1 in which the rubber latex is prepared by polymerisation of the monomers in aqueous emulsion in the presence of at least one alkali metal and/or ammonium sulphate and/or alkali metal and/or ammonium sulphonate containing 10 to 18 carbon atoms.
3. A process as claimed in claim 1 or claim 2 in which the polymerisation of the rubber latex is initiated by an organic peroxy-compound.
4. A process as claimed in claim 3 in which the organic peroxy-compound is an acylhydroperoxide; a diacylperoxide; an alkylhydroperoxide; an arylalkylhydroperoxide; a dialkylperoxide; a diarylalkylperoxide or a peroxyester, either alone or in combination with a reducing agent.
5. A process as claimed in claim 4 in which from 0.01 to 5% by weight of initiator, based on the total quantity of monomers, is used.
6. A process as claimed in any of claims 1 to 5 in which the polymerisation is carried out in the presence of a promoter.
7. A process as claimed in claim 6 in which the promoter is an inorganic metal salt the cation of which can exist in more than one valency state.
8. A process as claimed in claim 7 in which the promoter is a salt of copper, manganese, iron, cobalt or nickel.
9. A process as claimed in any of claims 1 to 8 in which the polymerisation is carried out in the presence of a chain transfer agent.
10. A process as claimed in claim 9 in which the chain transfer agent is tetrachloromethane; trichlorobromomethane; tetrachloroethane; methylallyl chloride; an alkyl or cycloalkyl alcohol; an alkyl mercaptan or a diisopropylxanthogenate.
11. A process as claimed in any of claims 1 to 10 in which the polymerisation temperature is from 5 to 60°C.
12. A process as claimed in any of claims 1 to 11 in which the heat sensitising agent is an organopolysiloxane consisting of two units of the formula



and 1 to 20 units of the formula



in which
X represents a group of the formula



R_1 represents hydrogen or an alkyl or aryl group,

R_2 represents an alkylene group which may contain oxygen,

R_3 represents a polyether group,

R_4 represents R_1 or an acyl group,

m represents 1 or 2 and n represents 1, 2 or 3.

13. A process as claimed in claim 12 in which the heat sensitising agent is used in a quantity of from 0.1 to 10% by weight, based on the solids content.
14. A process as claimed in claim 1 substantially as herein described with reference to any of the Examples.

15. A rubber latex when produced by a process as claimed in any of claims 1 to 14.

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